

RELEASE OF TRACE ELEMENTS FROM CCB: MAXIMUM EXTRACTABLE FRACTION

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Abstract

In EPA's recent regulatory determination, it was acknowledged that Coal Combustion By-Products (CCB) are a non-hazardous material and that increased utilization of this material should be encouraged. Environmental concerns about CCB focused on the potential release of trace elements to surface and groundwater, particularly when the material is used as mine backfill. A study at the U.S. DOE National Energy Technology Laboratory is quantifying the release of trace elements from CCB's in a column leaching experiment. A one kg fly ash sample is placed in each of seven 5-cm by 1-m acrylic columns. Leachants include deionized water, synthetic groundwater, synthetic precipitation, and 0.1 N solutions of acetic acid, sodium carbonate, sulfuric acid, and ferric chloride. Water is considered a control and the other fluids are surrogates for naturally occurring liquids. A single test consists of four different CCB samples connected to each of the seven leachant solutions. The material is leached at a nominal rate of 230 mL/d for between 24 days and 7 months until the leachate becomes acidic. The leachate is analyzed at 2 to 3 day intervals for major elements: iron, aluminum, calcium, magnesium, potassium, manganese, sodium. The leachate is also analyzed for the trace elements: antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, nickel, selenium, and zinc. Because the concentration of mercury is usually low in CCB and it is rarely detectable in the leachate, mercury is not routinely included as an analyte.

To evaluate the release of individual elements from the CCB samples, the cumulative quantity of each element (mg/kg) is calculated as a function of leachate volume. Generally, there is a short period of time when the volumetric leaching rate is at a maximum; then it decreases and approaches zero. If the volumetric leaching rate on the final day is less than 5 pct of the maximum rate, the amount leached from the sample is considered the total extractable concentration. This value is compared to the total concentration in the CCB sample to determine the maximum extractable fraction. Data have been evaluated for 36 fly ash samples. Variations in the maximum extractable fraction for various samples and for different leachant solutions may be related to the amount of amorphous material or to differences in mineral composition.

Introduction

In 1999, over 1 billion short tons of coal were mined in the US, and 90 % (942 million st) were used to generate electricity.¹ In an average year, 10 to 15% of the coal is recovered as coal combustion by-products (CCB), which include fly ash, bottom ash, boiler slag and flue gas desulfurization material (FGD). Fly ash, 60 % of CCB, is the finely divided residue from the combustion of coal collected by electrostatic precipitator (ESP) or filter (baghouse). Bottom ash consists of the heavier particles that fall to the bottom of the furnace and are removed as non-molten particles. Boiler slag is molten material that drains to the bottom of wet-bottom furnaces and is discharged to a water filled pit where it cools to form glassy particles resembling sand. FGD material is produced by processes that control sulfur emissions, such as wet scrubbers, spray dryers, sorbent injection.

The CCB are primarily the inorganic residue from coal; they contain elements such as iron, aluminum, magnesium, manganese, calcium, potassium, sodium and silica, and any carbon that was not consumed during combustion. CCB also contain small amounts (less than 1%) of other elements. These elements, generally referred to as heavy metals or trace elements (Table 1), are variously considered essential nutrients, toxic elements, or priority pollutants. Most of the elements in Table 1 are believed to have some environmental or public health consequences. The extent to which they can be released from the residues of coal combustion by naturally occurring fluids affects the suitability of CCB for various beneficial uses, like bulk fill and mine remediation.

Table 1. Concentration of Selected Elements in Fly Ash², mg/kg

Element	n ¹	Mean	Range	CV ² ,%
Arsenic (As)	39	156.2	7.7 - 1385	23
Barium (Ba)	39	1880	251 - 10850	126
Cadmium (Cd)	2	11.7	6.4 - 16.9	63
Chromium (Cr)	29	247.3	37 - 651	65
Copper (Cu)	39	185	44.6 - 1452	142
Nickel (Ni)	39	141	22.8 - 353	63
Lead (Pb)	39	170.6	21.1 - 2120	180
Antimony (Sb)	7	42.5	11 - 131	110
Selenium (Se)	30	14	5.5 - 46.9	69
Zinc (Zn)	39	449.2	27 - 2880	135

¹n = number of observations above the detection limit for a given variable in a set of 39 samples.

²CV Coefficient of Variation = Sample standard deviation divided by the sample mean

According to a survey by the American Coal Ash Association (ACAA), over 100 million st of

CCB were produced, and less than 30% was utilized, in 1998.³ Primary uses are in cement and concrete, as structural fill, and as road base. Less than 2% was used in agriculture and mine remediation. The remaining 70% of CCB was placed in landfills and ponds. Most of the CCB in the ACAA survey was produced from pulverized coal (PC) boilers.

On April 25, 2000, the Environmental Protection Agency (EPA) issued a regulatory determination governing the disposal and use of co-managed coal fired utility wastes, including fluidized bed combustion wastes.⁴ In a March, 1999 Report to Congress (RTC)⁵, EPA had tentatively concluded that disposal and most beneficial uses of such wastes should remain exempt from Subtitle C (hazardous waste) of the Resource Conservation and Recovery Act (RCRA). However, it was considering some form of regulation for fossil fuel wastes used in mine backfill although they had insufficient data to evaluate the environmental effects of this practice. The U.S. Department of Energy (DOE) submitted extensive laboratory and field data on the absence of environmental damage related to mine placement. During the internal government review prior to the final determination, DOE, the Office of Surface Mining Reclamation and Enforcement (OSM), and the U.S. Department of Agriculture (USDA) contended that: (1) there was no substantial evidence that CCB caused damage to health or the environment; (2) use in mine backfill was adequately addressed by current state and federal regulations; and (3) any classification of any coal combustion wastes as hazardous would significantly curtail all beneficial uses of this material. In April, 2000, EPA issued its Regulatory Determination, continuing to classify CCB as non-hazardous, although national regulations for CCB placed in landfills and surface impoundments are being considered. CCB used as backfill in surface and underground mines may also be subject to some form of regulation. A primary consideration in the need for regulation is the potential release of heavy metals (trace elements) from CCB when exposed to environmental fluids such as acid rain, groundwater or acid mine drainage. The DOE column leaching system generates data on the release of trace elements (heavy metals) under controlled conditions that can be used to evaluate the potential for surface or ground water contamination.

Experimental Methods

The DOE column leaching system is a continuous flow system that includes seven leachant solutions for simultaneous leaching of four different CCB samples.⁶ One kg samples of fly ash are placed in 5 cm by 1 m acrylic columns. The leachant solution flows through the column at a nominal rate of 250 mL/day; actual flow rates varied between 158 and 275 mL/d. Leachate samples, collected at 2 to 3 day intervals, are analyzed for pH, acidity and/or alkalinity, ferrous iron, total iron, aluminum, manganese, magnesium, calcium, sodium, potassium, sulfate and the trace elements: arsenic, barium, beryllium, cadmium, cobalt, chromium, copper, lead, nickel, antimony, selenium, and zinc. The discussion in this paper is limited to the extraction of these trace elements due to their environmental significance. Other elements, such as boron, molybdenum, silver, and mercury are not routinely included. Boron, molybdenum and silver increase the complexity and cost of analysis. The concentration of mercury in CCB is usually low, and the concentration in the leachate is frequently below the detection level. Screening tests for mercury indicated that the results didn't justify the additional analysis.

The leachants used in the column leaching test are described in Table 2. The leachant solutions

are intended to be surrogates for naturally occurring fluids, and represent all chemical types of leaching. All solutions were approximately 0.1 Normal.

Table 2 . Leachant solutions

Solution	Symbol	Formula	ID	Leach Type	pH
Deionized water	H ₂ O	H ₂ O	L1	Hydrolysis	6
Acetic Acid	HAc	CH ₃ COOH	L2	Acidic	2.88
Ammonium Hydroxide ¹	Base	NH ₄ OH	L3	Caustic	11.1
Sodium Carbonate	Base	Na ₂ CO ₃	L3	Caustic	12.1
Synthetic Ground Water ⁷	SGW	MgSO ₄ , H ₂ SO ₄ NaHCO ₃ CaSO ₄	L4	Hydrolysis	6.7
Synthetic Precipitation ⁸	SP	H ₂ SO ₄ , HNO ₃	L5	Acidic	4.2
Ferric Chloride	FeCl ₃	FeCl ₃	L6	Oxidative/Acidic	1.95
Sulfuric Acid	H ₂ SO ₄	H ₂ SO ₄	L7	Acidic	1.2

¹ Ammonium hydroxide was the caustic leachant in the first two tests. But to avoid potential formation of ammonia complexes which could complicate the interpretation of solubility results, sodium carbonate was used for all subsequent tests.

The system is designed to leach any material with a particle diameter of less than 0.5 cm. The samples tested to date include CCB samples from Pennsylvania, West Virginia, New Mexico, Florida, Maryland, Tennessee and Nevada. For this study, the intent was to obtain a random population of samples in order to quantify the general leaching characteristics. All samples are analyzed for major and trace elements (Table 3) by a commercial laboratory using ASTM standard methods. The discussion in this paper is limited to 36 samples, primarily power plant fly ashes, but also a bottom ash, an FBC fly ash, 2 non-utility boiler fly ashes and a fines from a steel processing slag.

Data Evaluation

Leachate samples are collected at intervals of 1 to 3 days and analyzed. The data are initially assembled as concentration of each analyte in mg/L versus elapsed time in days for each leachant solution (Fig. 1). After correcting for a blank, the concentrations were converted to the cumulative amount of each element removed from the sample. On a cumulative basis, it is possible to compare the removal of an element from the CCB sample in all leachant solutions (Fig. 2). Generally, the rate of extraction is relatively slow until some point at which there is a steep increase in the cumulative curve. Then the rate of extraction tends to decrease. When the slope of the cumulative curve approaches zero, extraction is considered complete.

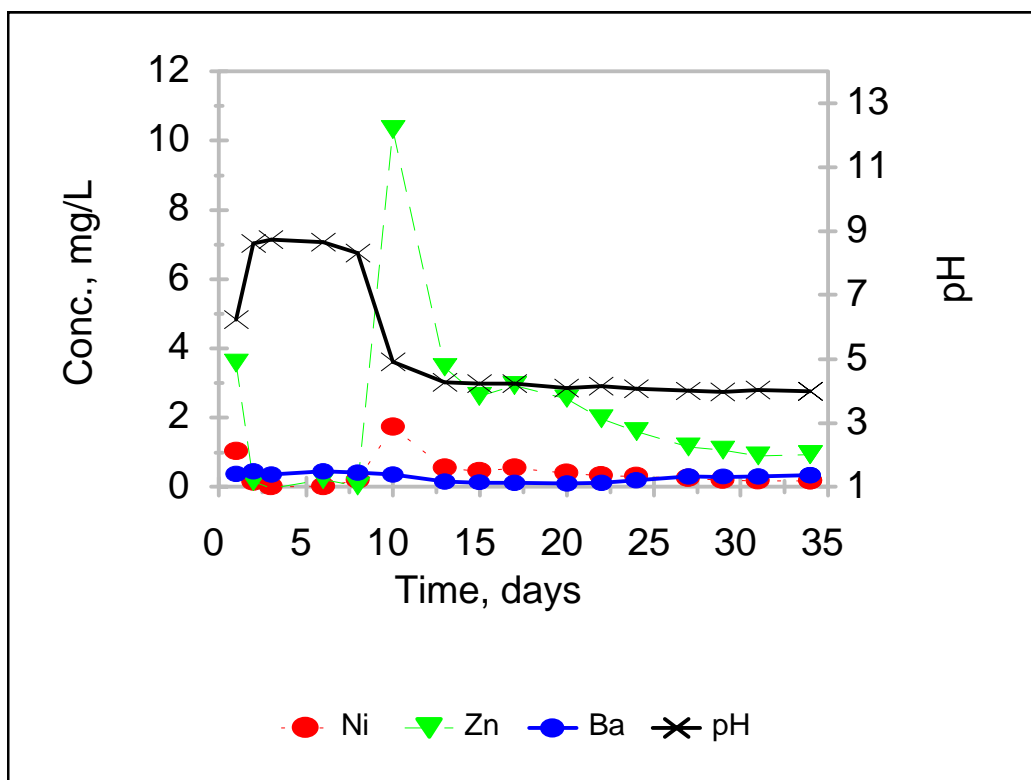


Figure 1. Sample # 17:L1 - Time dependent change in concentration of leached elements and pH.

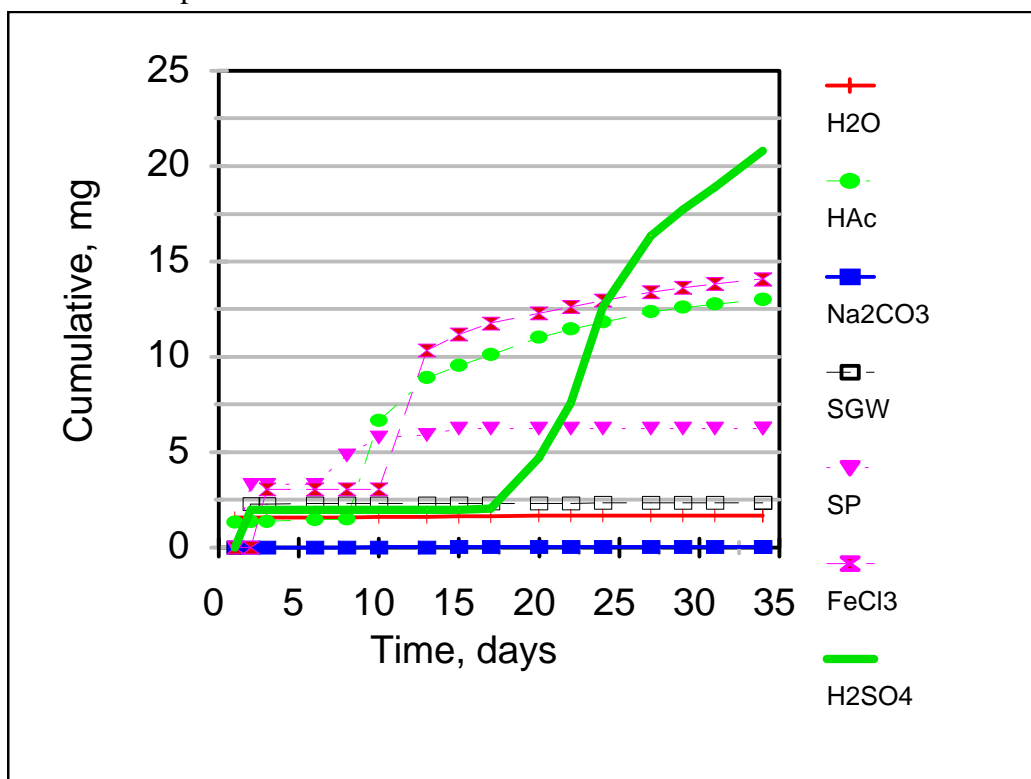


Figure 2. Cumulative extraction of zinc from Sample # 17. $C_{mx} = 21$ mg/kg. $C_s > C_{mx}$. C_s not determined in this test.

For each element, the extractable concentration (C_{mx}) was set at the highest value determined for any leachant solution. To determine if leaching had reached an endpoint, the slope of the cumulative concentration curve was calculated as a function of the leachate volume, i.e., the leachate rate with respect to volume. If the final rate was less than 6 pct of the maximum rate, extraction was considered complete. The soluble concentration (C_s) was equal to the maximum extractable concentration if leaching was complete. The soluble concentration was not determined if any of the concentrations in other leachants were higher than that in the solutions in which leaching had been completed.

The extractable fraction was calculated as the amount extracted from the sample (mg/kg) divided by the concentration in the solid (mg/kg). Although it was the preferred variable since it eliminated variability due to differences in concentration of a metal in the solid, it could not be calculated if the concentration in the solid was below the detection limit. If leaching was completed for the highest value obtained ($C_{mx} = C_s$), then the maximum extracted fraction (MEF) was calculated by dividing the soluble concentration (C_s) by the concentration in the solid (C).

Results

The pH of the leachate was affected by the alkalinity of the CCB sample. Many of the trace elements were apparently most soluble in acid; the concentration of the element increased as the pH of the leachate decreased. Concentration in the leachant solution usually reached a maximum, then decreased as the pH of the leachate approached a constant value. From the cumulative concentration curve for an element, it was readily apparent if leaching had reached an end point and which leachant solution was most effective at removing that element from that sample. For a given sample, the cumulative concentration curves were evaluated to determine the total leached concentration (C_l) in each leaching solution. The maximum concentration (C_{mx}) of an element was the highest value of C_l . The most effective leachant solution (L_{mx}) was that which had extracted the highest concentration of that element from that sample. If the extraction of the element had reached a solubility limit, C_{mx} was equal to C_s .

Based on this analysis, it was noted that elements were preferentially leached by one type of solvent (Column 2, Table 4). The next column in Table 4 shows the percentage of samples in which C_{mx} was measured in the dominant leachant type. The percentage of samples in which that element was leached to an apparent solubility end point in all leachant solutions is given in column 4. The last column lists the percentage of samples that were leached to an endpoint in the dominant leachant solution. For example, considering all samples and all leachant solutions, arsenic was leached to an endpoint in 52% of the tests. In other words, in 131 of 252 leaching combinations (36 samples in 7 leachant solutions), arsenic was leached to an endpoint. Considering only the dominant leachant (Column 5, Table 2), sodium carbonate, in only 48% of these 36 samples arsenic was completely leached.

Table 3. Trace element concentrations in CCB samples, mg/kg

Sample #	As	Ba	Be	Cd	Co	Cr	Cu	Ni	Pb	Se	Zn
2 ¹	<100	95	<5	<25	<50	<50	<25	<50	<50	2.3	11
3 ¹	<100	76	9	<25	<50	<50	51	59	<50	90.7	43
4	<100	121	<5	<25	<50	<50	<25	<50	<50	5	16
5	<100	155	<5	<25	<50	<50	<25	<50	<50	4.4	23
6	171	1140	11	<10	41	175	114	107	90	4.8	201
7	166	1090	10	<10	39	170	105	107	64	4.8	191
8	67	855	8	<10	31	171	74	1040	59	2.8	135
9 ²	<40	321	<2	<10	<20	5970	95	710	29	2.1	75
10	<200	3310	<10	<10	<100	<100	50	<100	<100	7.3	65
11	<200	859	<10	10	<100	173	115	<100	113	11	202
12	<200	893	<10	<10	<100	165	119	<100	112	9.6	207
13	<200	866	<10	<10	<100	164	112	<100	109	11.6	188
14	<100	456	12	15	40	184	93	124	71	7.6	175
15	229	844	14	15	42	185	158	106	124	8.5	235
16	301	1160	13	15	42	170	139	109	121	7.8	204
17	<100	471	<5	<15	<25	132	72	71	81	17.7	204
18	77	529	2	<1	11	97	76	85	<1	1.4	124
19	125	511	6	<1	16	111	76	92	<1	1.8	155
20	277	1380	10	<1	44	110	155	135	<1	1.6	197
21	148	849	12	<1	31	92	122	125	<1	1.9	128
22	29	1520	<.05	<1	<.5	53	71	37	<1	3.7	46
23	44	999	<.05	<1	<.05	55	42	35	<1	3.2	33
24	53	789	14	<1	59	176	152	120	134	1.9	113
25	143	699	4	<1	23	136	74	84	116	3.7	136
26	44	469	6	1.1	33	114	53	124	12	1.4	34
27	28	765	18	<5	86	176	156	137	65	8.6	112
28	69	703	19	<5	79	211	176	131	99	7.8	121
29	142	2010	26	<5	76	179	246	149	110	17.5	112
30	90	781	11	<.1	50	205	117	119	24	13.3	139
31	175	951	27	<.1	73	193	255	171	109	19.6	252
32	104	721	11	6.4	25	183	76	124	116	16.1	438
33	91	892	9	<.1	42	181	79	101	77	8.6	140
34 ³	106	268	15	0.7	31	87	108	126	65	20	333
35 ³	52	647	4	1.5	28	129	53	1330	40	3.3	33000
36	144	1070	19	1.8	21	174	1610	482	173	18.7	609
37 ⁴	29	1110	9	0.2	26	119	6130	199	762	0.4	600

¹ Non utility fly ash² Steel slag fines³ FBC fly ash⁴ Bottom ash

Note: No analytical data is available for the concentration of antimony (Sb) in the CCB

Table 4. Comparison of dominant leachant solution and samples leached to solubility endpoint.

T r a c e Element	L _{mx} Type	% Samples C _{mx} / L _{mx}	% Samples C _{mx} = C _s	% Samples C _{mx} = C _s and L = L _{mx}
Arsenic	Caustic	87	52	48
Barium	Oxidative	67	17	21
Beryllium	Acidic	94	22	20
Cadmium	Acidic	100	67	67
Cobalt	Acidic	91	20	19
Chromium	Acidic	61	22	18
Copper	Acidic	67	36	38
Nickel	Acidic	72	14	15
Lead	Oxidative	60	40	20
Antimony	Caustic	47	100	100
Selenium	Caustic	47	95	100
Zinc	Acidic	72	42	38

For over 50% of ions, the most effective leachant solution is an acid, either sulfuric or acetic (Fig.3). When the leachant are grouped by type of leaching, the dominance of acidic leaching is more pronounced (Fig.4). Some elements, barium and lead, also have a relatively high percentage of the oxidizer, ferric chloride, as the most effective leachant. Arsenic, selenium and antimony are most effectively leached by the caustic leachant solution.

Some elements in some samples were insoluble in all leachant solutions (Table 5). However, no sample was completely insoluble. Individual elements could be insoluble in some but not all of the leachant solutions. For example, arsenic in five CCB samples was insoluble in all leachant solutions. In an additional 13 samples, it was insoluble in water (L1). In only 3 samples was arsenic insoluble in sodium carbonate (L3) but soluble in some other leachant. Barium was the only element that was soluble in all samples in all leachants.

Table 5. Number of samples with insoluble elements in various leachant solutions.

ELEMENT	L = All	L1	L2	L3	L4	L5	L6	L7
Arsenic	5	13	9	3	14	15	9	10
Barium	0	0	0	0	0	0	0	0
Beryllium	4	20	2	16	24	23	8	4
Cadmium	0	11	8	21	17	19	10	0
Cobalt	1	7	1	14	11	18	8	4
Chromium	0	1	0	1	1	1	17	2
Copper	0	6	4	13	16	8	14	7
Nickel	0	0	0	3	2	5	9	2
Lead	11	17	20	23	22	20	9	9
Antimony	6	20	14	12	9	21	16	21
Selenium	17	6	10	4	11	10	6	10
Zinc	0	0	0	0	0	0	7	0

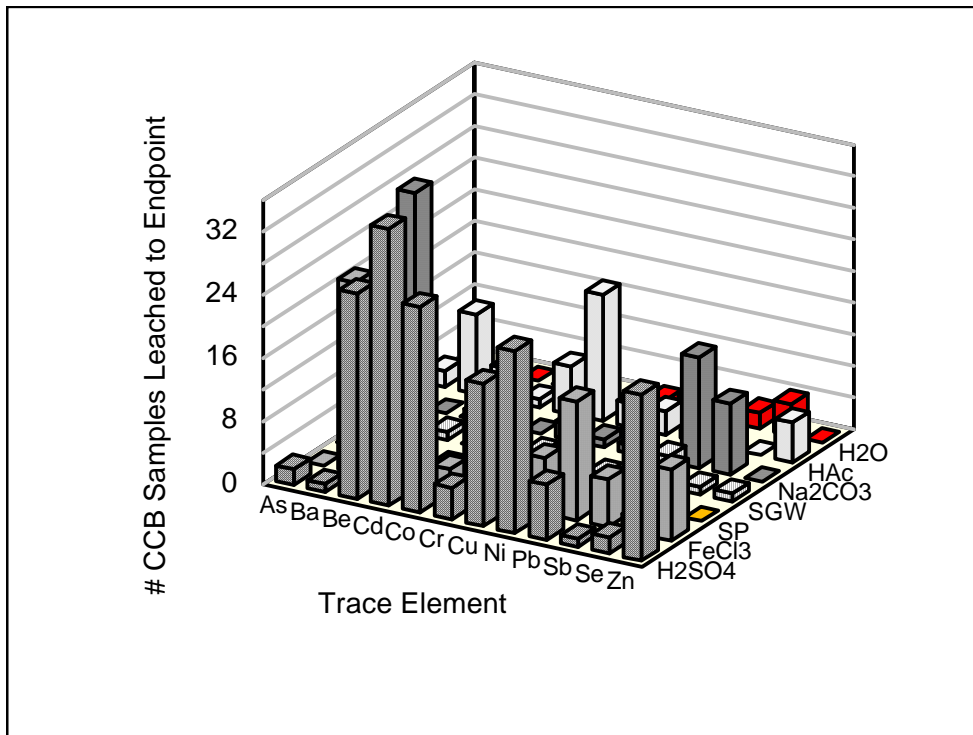


Figure 3. Number of samples in which trace element was leached to endpoint by various leachant solutions.

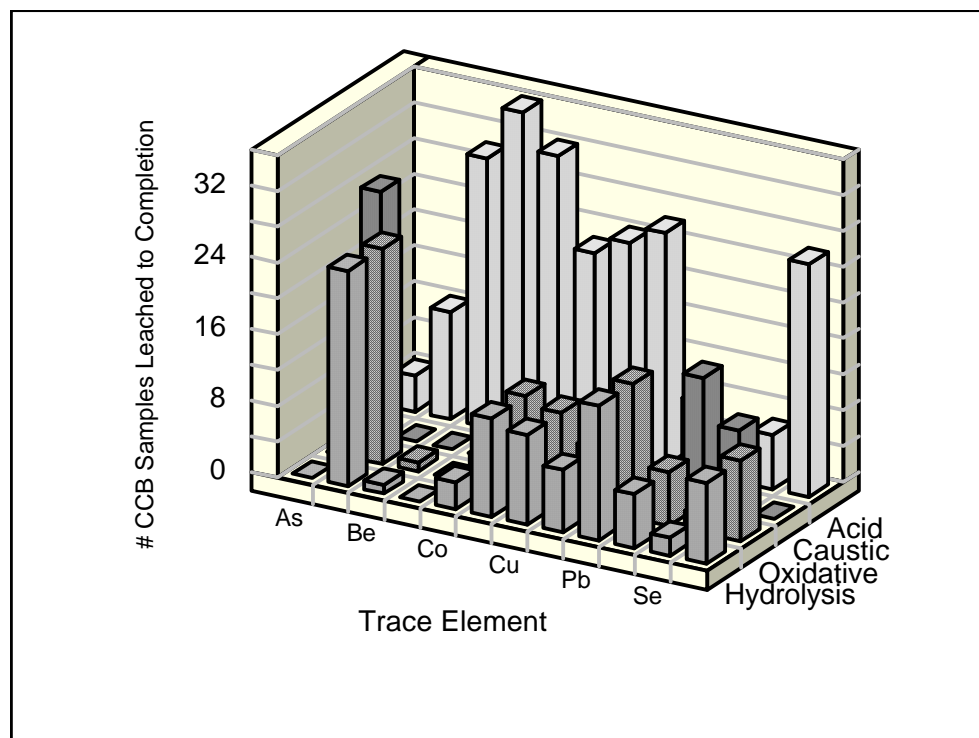


Figure 4. Number of samples in which trace element was leached to completion by type of leachant solution

For each sample, the cumulative concentration of each element leached in each leachant solution was calculated. Whether the solubility end point had been reached was evaluated from the cumulative concentration curve. For sample/element combinations, the maximum leached concentration at a solubility end point (C_s) is listed in Table 6. The leachant solution (L_{mx}) in which C_s is measured is also given. Blank cells in Table 4 indicate that the solubility end point was not reached in any leachant solution. A zero value indicates that the element was insoluble in all leachant solutions.

The maximum extractable fraction (Table 7) was determined as the maximum soluble concentration (mg/kg) divided by the concentration of the element in the CCB sample (mg/kg). The extractable fraction could not be determined for those samples in which the concentration in the solid was below detection limits. The values in Table 7 represent those element/sample combinations for which the maximum extracted concentration was also a solubility end point and for which the concentration of that element in that sample was known.

The fraction of an element that was soluble was variable, generally from less than 1% to 50%. The average maximum solubility of an element was usually less than 50%. Notable exceptions were cadmium and selenium; in several samples, the leached concentration apparently exceeded the concentration in the solid sample. Whether this was due to inaccuracy in sampling and/or the analytical procedure has not been determined.

When evaluated across all samples, there is no apparent equivalence in the extractable fraction of any of the element measured. There is also little consistency in the solubility of the elements in various CCB samples.

Discussion

The most obvious inference from the leaching tests is that the trace elements in CCB act like independent variables. Three of the elements, arsenic, antimony and selenium are most soluble in the caustic leachant solution. However, arsenic in approximately 17 % of the samples is insoluble in the high pH leachant. The amount of arsenic leached in acid is about 4% of the maximum extracted concentration, but between 30 and 60 % of the caustic leached concentration when the solubility end point was not reached. The concentration of antimony in the solid was below detection limits for all samples. The extraction of antimony reached the solubility limit for all samples, and the average cumulative concentration was less than 1 mg/kg. Selenium was apparently insoluble in all leachants in over 60% of the samples. Selenium was twice as soluble in water as in acid.

Barium in all samples was soluble in all leachant solutions. It was apparently most soluble in the ferric chloride; however, this may be an artifact of the acidity of the ferric chloride. Barium sulfate, which would be produced by reaction with sulfuric acid, is insoluble and may have precipitated within the column. The solubility of barium in acetic acid is approximately 90% of the ferric chloride solubility, indication that acid leaching is the more probable mechanism.

Table 6. Maximum concentration, mg/kg, at solubility end point ($C_{mx} = C_s$) and most effective leachant solution (L_{mx})

Sample #	As		Ba		Be		Cd		Co		Cr		Cu		Ni		Pb		Sb		Se		Zn	
02			28.34	L6	1.16	L7	3893.04	L7	3.32	L7	14.39	L6	10.88	L7	9.31	L7	45.67	L7	0.42	L7	0.00		783.22	L2
03	27.73	L3			3.83	L7	4298.80	L7	11.62	L7			22.46	L7	13.72	L7			0.37	L3	0.00		41.22	L6
04	0.49	L2	10.20	L7	0.63	L2	7.87	L7									0.28	L2	0.53	L2	0.00		21.86	L7
05	0.00						173.43	L7											0.30	L1	0.00			
06							1756.35	L7											0.64	L6	1.64	L3		
07							4085.07	L7											0.70	L6	0.95	L1		
08	1.66	L7																	0.00		0.00			
09	0.00				0.00		0.95	L7	0.11	L7			0.06	L7	0.11	L1	0.00		0.00		0.00			
10	0.00																0.00		0.07	L4				
11													11.42	L6					0.16	L6	8.86	L6		
12																			0.12	L4	0.76	L1		
13																			0.28	L6	0.82	L3		
14							142.83	L7									0.00		0.44	L3	0.00	L1	19.81	L6
15											8.75	L2	21.24	L6					1.54	L3			53.47	L6
16	182.50	L3					446.39	L7											0.87	L3	0.00		93.83	L7
17							874.58	L7									0.00		0.50	L6	0.00			
18	13.20	L3					2955.69	L7											0.21	L6	0.00		24.75	L2
19					0.69	L7	307.66	L7					3.05	L7			0.00	L1	0.07	L4	0.00			
20	44.19	L3												L1			0.06	L4	1.21	L3	0.26	L7		
21					0.93	L7	176.43	L7	1.29	L7			3.98	L7	3.22	L7	0.00		0.31	L3	0.00		10.94	L7
22	1.96	L3			0.00		0.48	L7	0.02	L2	10.74	L3	0.16	L1			0.01		0.08	L1	0.61	L3	3.55	L6
23	0.25	L2	180.36	L6	0.00		8.01	L7			2.07	L3	0.00	L5			0.00		0.09	L2	0.51	L5	22.40	L7
24	27.01	L3	129.74	L6			1962.37	L7			33.99	L6	35.05	L7			12.02	L6	1.00	L3	0.00		49.96	L6
25	45.33	L3					645.32	L7									0.31	L7	0.11	L2	0.22	L1		
26	11.50	L3					1353.32	L7	0.86	L6							0.00		0.00		3.20	L3	7.52	L2
27							27.89	L7											0.44	L3	12.24	L3		
28	28.88	L3	34.25	L6			107.79	L7			14.95	L2	15.13	L6			1.45	L6	1.03	L3	9.17	L3	13.19	L7
29	69.73	L3					106.96	L7									0.00		0.98	L3	12.02	L1	11.15	L2
30	26.71	L3					158.90	L7									0.00		0.01	L4	2.95	L3		
31	85.53	L3					296.09	L7											1.25	L3	4.51	L3		
32																	0.34	L6	0.31	L3	7.43	L3		
33							107.85	L7											0.00		1.20	L6		
34	0.00				0.00	L1			0.00								0.00		0.00					
35	0.00		46.90	L6	0.00	L1			0.05	L7	0.02	L5	0.02	L5	1.25	L7	0.00		0.00					
36					4.20	L7					18.36	L7							1.64	L3	3.37	L4	114.83	L7
37	3.97	L3											50.21	L7			2.37	L7	0.56	L3	0.00	L1		

Table 7. Maximum Extracted Fraction

Sample #	As	Ba	Be	Cd	Co	Cr	Cu	Ni	Pb	Sb	Se	Zn
02		0.298									0.000	71.202
03			0.425				0.440	0.233			0.000	0.959
04		0.032							0.010		0.000	1.366
06											0.341	
07											0.199	
08	0.010				0.000						0.000	
09	0.000		0.000		0.004		0.001	0.000	0.000		0.000	
11							0.099				0.805	
12											0.079	
13											0.070	
14				9.522					0.000		0.000	0.113
15					0.000	0.047	0.134					0.228
16	0.606			29.759							0.000	0.460
18	0.171										0.000	0.200
19			0.115				0.040				0.000	
20	0.160				0.000						0.162	
21			0.078		0.041		0.033	0.026			0.000	0.086
22	0.067					0.203	0.002				0.164	0.077
23	0.006	0.181				0.038	0.000				0.160	0.679
24	0.510	0.164				0.193	0.231		0.090		0.000	0.442
25	0.317								0.003		0.058	
26	0.261			1230.291	0.026				0.000		2.283	0.221
27											1.423	
28	0.419	0.049				0.071	0.086		0.015		1.176	0.109
29	0.491								0.000		0.687	0.100
30	0.297								0.000		0.222	
31	0.489										0.230	
32					0.000				0.003		0.462	
33											0.139	
35	0.000	0.072	0.000		0.002	0.000	0.000	0.001	0.000			
36			0.221		0.000	0.106					0.180	0.189
37	0.137				0.000		0.008		0.003		0.000	

Beryllium in 1/3 of the samples was insoluble in acid leachants and 2/3 of the samples were insoluble in other leachant solutions. The leachable concentration was less than 10 mg/kg in sulfuric acid and less than 1 mg/kg in other leachants.

Cadmium in all samples was soluble in sulfuric acid, but as many as 50 % of the samples were insoluble in other leachant solutions. The solubility limit was approximately 1000 mg/kg in sulfuric acid and less than 1 mg/kg in the other leachant solutions. Cobalt in about 1/2 of the samples is also insoluble in non-acid leachants. All samples were leached to a cobalt solubility endpoint in water, and the maximum solubility was less than 3 mg/kg.

Chromium in 50% of the samples was insoluble in ferric chloride, but in the other 50% of the samples it was most soluble in that leachant solution. Its acid solubility was less than 2/3 of the solubility in ferric chloride. Copper in 1/3 samples was also insoluble in ferric chloride, but very soluble in other samples. The sulfuric acid solubility for these samples is about 90% of the ferric chloride solubility. Nickel shows similar solubility patterns with respect to ferric chloride. Copper and nickel solubility is approximately 1 mg/kg in non-acid leachants.

Lead in 50% of the samples is insoluble in all leachants. The extracted concentration of lead is less than 1 mg/kg in all leachants but ferric chloride and sulfuric acid. In contrast, zinc in almost all samples is soluble in all leachants, but is most soluble in acid leachants.

The observed leaching behavior of the twelve trace elements from 36 samples strongly supports previous studies on solid composition that CCB are highly variable.⁹ Other studies have also noted the apparent dependence of the solubility of trace elements on pH.¹⁰ The leaching characteristics of CCB may be related to the modes of occurrence of these elements in the original coal. Researchers at the USGS have developed a sequential leaching procedure for coal samples to estimate the mineral with which trace elements are associated.¹¹ They related insolubility to the association with silicates, primarily clays or quartz. The presence of these minerals in CCB may explain differences in trace element solubility. The temperature at which ash particles are formed has also been indicated in leachability.¹²

Summary

Based on the results of this study and others, it is apparent that the release of trace metals from CCB cannot be described by a simple solubility relationship that is only a function of the concentration in the solid and the volume of the leachant solution. The mineral phases present in the CCB may control solubility. Solubility may also be a function of the ratio of soluble crystalline to insoluble amorphous phases in CCB. The distribution of an element in different mineral phases, which may be related to the original coal minerals, the temperature of combustion, and the cooling rate, is also a factor that may explain differences in solubility.

Additional evaluations of the factors that control the solubility of trace elements from CCB will focus on the determination of mineral phases, as well as determination of the concentration of trace elements in the solid if the original analysis indicated that these were below the detection level. The solubility endpoint will also be estimated from the original concentration versus time leaching curves for all elements that were not leached to completion.

Even though analysis of the data from this leaching study has not yet determined a general pattern to the solubility of trace elements from CCB or been able to characterize the factors that control leaching, it has shown that the solubility of trace elements is relatively low. In general, the release of trace elements from CCB is not expected to present a hazard when these materials are exposed to naturally occurring fluids.

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